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(71) Applicant: CALIFORNIA INSTITUTE OF TECHNOLOGY [US/US]; 1200 East California Boulevard, Pasadena, CA 91125 (US).

(72) Inventors: KINDLER, Andrew; 616 Plymouth Road, San Marino, CA 91108 (US). LEE, Albany; 20 E. Camino Real Avenue, Arcadia, CA 91006 (US).

(74) Agent: HARRIS, Scott, C.; Fish & Richardson P.C., Suite 1400, 4225 Executive Square, La Jolla, CA 92037 (US).

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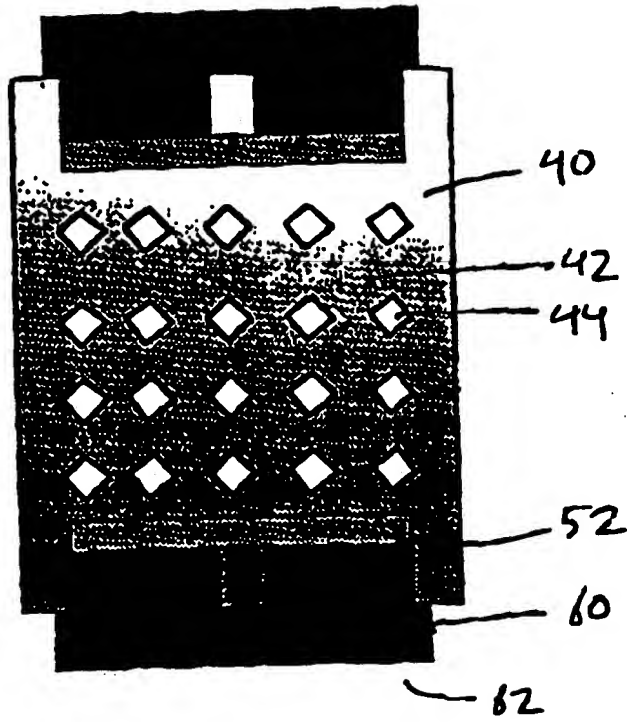
(54) Title: FUEL CELL ELEMENTS WITH IMPROVED WATER HANDLING CAPACITY

(57) Abstract

New fuel cell components for use in liquid feed fuel cell systems are provided. The components include biplates (70) and endplates (40), and allow high efficiency operation. Conductive elements (44) and a wicking device (60) also form a part of the fuel cell components of the invention.



FUEL CELL ELEMENTS WITH IMPROVED WATER HANDLING CAPACITY

Statement as to Federally Sponsored Research

The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 U.S.C. 202) in which the Contractor has elected to retain title.

Field of the Invention

The invention relates to the methods and apparatus of generating energy through low-cost, efficient processes. More specifically, the invention relates to components of a fuel cell for generating electricity.

Background of the Invention

Methanol fuel cells promise to provide efficient and low-cost electrical current from methanol without burning the fuel. Therefore, pollution from combustion is not created by the use of such fuel cells. The fuel cells can be at least as efficient as gasoline engines; they run cool, without the need for insulation and structural reinforcement; and rely on a relatively inexpensive fuel. The methanol fuel cells which were designed initially produced about 100 W, running up to 200 continuous hours, and up to 3,000 intermittent hours, without suffering any

which has the functional effect of making the biplate an extremely hydrophobic surface.

At this time, cost is the major factor limiting methanol fuel cell commercialization. One difficulty in the operation of methanol fuel cells is the water that normally accumulates in the channels of the cathode side of the biplate. The source of this water can be from the chemical reaction of the fuel cell, it can be a result of electroosmosis from the anode side, or it can be a result of simple diffusion. If the accumulated water is not removed, the performance of the fuel cell can suffer. The traditional way to remove this accumulated water has been by pressurized air.

It is desirable to design fuel cell systems which work at temperatures between 25 and 45°C. However, the power output of methanol fuel cells at 25°C is only about 15-20% of the same cell operating at 90°C. Thus, it becomes important to reduce the energy consumption of ancillary processes as much as possible. For example, power consumption of a pressurized air delivery system can unacceptably diminish the advantages of a room temperature methanol fuel cell. It is considered desirable to design such cells so as to minimize the air flow required to remove accumulated water.

prevent fluid communication between the adjacent negative and positive electrodes of a fuel cell. A biplate may also prevent fluid communication between the last compartment of a fuel cell in a stack and the exterior of the fuel cell. This last aspect of the definition of biplate includes the specific fuel cell components which are found at each end of a stack of cells, also referred to as the endplates. "Endplates" are merely biplates which are not between fuel cell compartments, but are found at the terminus of a fuel cell stack.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. All publications, patent applications, patents and other references mentioned herein are incorporated by reference in their entirety. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods and examples are illustrative only and not intended to be limiting.

solution separates the electrodes. When the cell is discharging (converting chemical to electrical energy), an oxidation reaction occurs at the negative electrode (anode). At the positive electrode (cathode), a reduction reaction occurs during discharging.

For the electrode reactions of any corresponding pair of anode and cathode (an electrochemical couple), electrons pass through the external circuit from the anode to the cathode. Completion of the circuit occurs when ionic species are transferred across the cell through the intervening electrolyte. The change from electronic conduction to ionic conduction occurs at the electrodes and involves an electrochemical (Faradaic) reaction. However, electrons cannot pass through the electrolyte, or short circuiting will result in cell self-discharge.

The reactions described above consist of a sequence of more elementary and microscopically scaled steps. In any case, the reactants must approach each other within molecular distances, and the products must be continuously removed for the cell to operate properly. Electrons from the external circuit must reach or leave the reaction sites. Therefore, the reaction sites must be electrically connected to the external circuit. Typically, ionic species must migrate toward or away from the reaction site. Concentration variations can therefore affect reaction

where H is the enthalpy (heat content), S is the entropy, and T is the temperature. The cell potential U is related to the free energy change as follows:

$$\Delta G = -n F U$$

where ΔG is the free energy change for the overall cell reaction based on the reversible transfer of n equivalents of electrons, and F is the Faraday constant. This relation holds in the absence of corrosion reactions.

Conventional methanol fuel cells generate water on the cathode side of the cell compartments through several processes. This water needs to be removed continually for the efficient operation of such cells. Pressurized air or oxygen was required to remove the water by blowing across the cathode surface. The energy required to remove this water lowered the efficiency of methanol fuel cells, particularly at low temperatures (from 25°C to about 45°C), where the fuel cells are least efficient, and energy losses are felt most keenly.

It has been noted by the present inventors that fuel cell components can be made in such a way as to minimize the energy needed to remove water from the cathode surface of such components. Fuel cell systems utilizing such

described below, illustrates a particular embodiment of a fuel cell system incorporating a stack of individual fuel cells including the re-circulation system. The following detailed description of the fuel cell of Fig. 1 primarily focuses on the structure and function of anode 14, cathode 16 and membrane 18.

Prior to use, anode chamber 22 is filled with the organic fuel and water mixture and cathode chamber 28 is filled with air or oxygen. During operation, the organic fuel is circulated past anode 14 while oxygen or air is pumped into chamber 28 and circulated past cathode 16. When an electrical load (not shown) is connected between anode 14 and cathode 16, electro-oxidation of the organic fuel occurs at anode 14 and electro-reduction of oxygen occurs at cathode 16.

At the anode, a fuel and water mixture flows at a flow rate of from about 10 to about 500ml/minute, and the following reaction takes place.

$$\text{Anode:} \quad CH_3OH + H_2O \rightarrow CO_2 + 6\ H^+ + 6\ e^-$$

Carbon dioxide produced by the above reaction is withdrawn along with the fuel and water solution through outlet 23 and separated from the solution in a gas-liquid separator (described below with reference to Fig. 2). The

well known in the art as providing activated surfaces upon which these reactions can take place. Preferred catalysts for the methanol fuel cells of the invention are platinum/ruthenium catalysts. A carbon supported catalyst is preferred because catalyst consumption is thereby minimized, and adhesion to the substrate is increased.

Membrane 18 can be formed from NAFION™ (a copolymer of tetrafluoroethylene, and perfluoropolyether sulfonic acid), modified perfluorinated sulfonic acid polymer, polyhydrocarbon sulfonic acid or composites of two or more kinds of proton exchange membranes.

Anode 14 can be formed from platinum-ruthenium alloy particles either as fine metal powders, that is, "unsupported", or dispersed on high surface area carbon, that is, "supported". Other platinum-based alloys include those made with tin, iridium, osmium or rhenium as the second metal. For platinum-ruthenium, the loading of the alloy particles in the electrocatalyst layer is preferably in the range of 0.5 - 4.0 mg/cm^2.

Cathode 16 is a gas diffusion electrode in which platinum particles are bonded to one side of membrane 18, and is preferably formed from unsupported or supported platinum bonded to a side of membrane 18 opposite to anode 14. Typically available materials and methods of fabrication for the above components are given, for example,

into circulation tank 35. Hence, circulation tank 35 receives both a fuel and water solution from injection unit 29 and a fuel and water solution from heat exchanger 37. Circulation tank 35 extracts carbon dioxide from the fuel and water mixture and releases the carbon dioxide through vent 39. The resulting fuel and water solution is fed through pump 20 and into stack 25. Circulation tank 35 can also be located between stack 25 and heat exchanger 37 so as to remove the carbon dioxide before the heat exchanger and thereby improve the performance of the heat exchanger. Further details are provided, for example, in U.S. Patent 5,599,638.

Since water is a product of the reaction, high efficiency depends on the removal of water as it accumulates in fuel cell compartments. The present invention is based on allowing gravity to efficiently drain water from the fuel cell. As will be detailed below, proper design of the fuel cell will allow the removal of water to proceed with very high efficiency.

Biplate and Endplate

The biplate is a two-sided separator which prevents contact between the negative and positive electrodes of the fuel cell. In many embodiments, the biplate will be substantially planar, with a positive electrode on one side

use in the methanol fuel cells of the invention are 97% water and 3% methanol.

The inventors noted that water tends to accumulate in fuel cell compartments at or near the cathode. For efficient fuel cell operation, this water is desirably continuously removed.

According to a particular embodiment, the plates of the liquid feed fuel cells are provided with a hydrophilic surface. Such surfaces have the desirable property of discouraging droplet formation, and allowing the formation of a sheet of water which is more easily drained by gravity. Thus, as soon as water is released at the cathode, it becomes part of a liquid layer that drains to the bottom of the biplate or endplate.

Hydrophilic plate surfaces are not difficult to create, but are difficult to maintain as hydrophilic. Such surfaces are high energy surfaces, and are therefore more reactive than hydrophobic surfaces. Although the claims are not limited by any particular theory, it is believed that air-borne organic contaminants can be absorbed or adsorbed onto such surfaces, causing them to become hydrophobic. Within an hour or so after creating a freshly sputtered metal surface, typical contaminants in the air result in a hydrophobic surface being created on typical fuel cell plates. According to the embodiment, hydrophilic plate

the deposition of a first layer, but not roughened to a degree which would lead to an uneven hydrophilic surface, after completion of the preparation of this surface.

Hydrophilic materials to be applied as a first layer, include polymeric materials. These hydrophilic polymeric materials can be applied by any of the above-mentioned methods, including formation of such a layer *in situ* such as by polymerization on the roughened surface. Desirably, such materials are applied as liquids and are allowed to dry to a solidified state.

Examples of hydrophilic materials which can be applied to the plate surfaces include fluoropolymers such as perfluoropolyether sulfonic acid; polystyrenes such as polystyrene carboxylic acid and polystyrene sulfonic acid; polyallylamine; linear and branched polysaccharides such as dextran, pullulan, and polymaltotriose; cellulose and derivatives such as hydroxypropyl cellulose; acrylic acid polymers and acrylamide polymers including alkyl substituted acrylamides such as N,N-dimethyl acrylamide, polymethacrylic acid, N-isopropyl acrylamide, and the like; polyethylene oxides including hydroxy and methoxy terminated polyethylene oxides; polyethylene glycol, polypropylene glycol; polyvinyl compounds such as polyvinyl acetate, polyvinyl alcohol and polyvinyl butyral; polypyridine and polypyridinium compounds such as poly-2-vinyl-N-methyl pyridinium halide, poly-4-

carbon/metal layer is applied. Desirably, this layer is applied as a finely divided solid.

Suitable materials include carbon/metal composites such as carbon-supported catalysts including carbon-supported platinum, palladium, platinum/palladium, platinum/palladium/gold, platinum/tin, platinum/rhodium, platinum/ruthenium, palladium/ruthenium, and many other carbon/metal composites.

The inventive plates have two further features to facilitate the removal of water from the fuel cell compartment.

First, the exit port is made large enough that water cannot significantly block the flow of air. For this reason, the water does not require a significantly greater amount of air or oxygen pressure to remove such unwanted water than would be required in the absence of such water. Such an exit port can be made by removing material from the plate, for example as is shown in Fig. 3.

Fig. 3 shows a particular embodiment of inventive fuel cell plate 40. The plate has flowfield 42, which includes conductive elements 44, embodied in Fig. 3 as pins (some pins have been removed for clarity of illustration). Also indicated is air flow path 46, which is generally perpendicular to plate 40, and directed through flowfield 42. Plate 40 also has circumferential rim 48, which forms a

size, and subsequently drop into a separate collection vessel by the force of gravity. These droplets are not in the air flow stream, so they do not significantly contribute to flow resistance.

Such an insert is a surface which can be directly contiguous with the surface of the biplate or endplate. Alternatively, the insert is a surface which can be indirectly contiguous with the biplate or endplate surface, by means of an intermediate surface which leads a liquid from the biplate surface to the insert surface. This acts to extend the sheet of liquid which is present on the hydrophilic plate surface to allow droplet formation at a point where it does not interfere with the air flow path. Such an arrangement is illustrated in Fig. 4.

Fig. 4 shows plate 40 with conductive elements 44 which make up flowfield 42. At the edge of plate 40 is surface 52, which creates an expanded channel for exit port 50. Also included is insert 60, which extends from plate 40. Lower edge 62 of insert 60 allows a surface on which water can collect. The surface is out of the path of air flow, which moves through flowfield 42 and through exit port 50.

Fig. 5 shows an end view of plate 40 with insert 60 attached. Included are insert supports 64, which add strength to the assembly. Flowfield 42 is viewed edge-on in

of the plate. As noted above, the biplate itself does not need to be conductive. The conductive elements can be arranged in any suitable pattern throughout the biplate. In some preferred embodiments, a plurality of such conductive elements define what is referred to as a "pincushion" pattern of conductive elements. Fig. 6 shows plate 40, which can be a biplate or endplate, having a particular embodiment of pincushion flowfield 42 made up of conductive elements 44. Fluid flow direction 66 is indicated. The "pincushion" can extend to both sides of the biplate.

Fig. 7 is a side view of biplate 70, with a particular embodiment of a pincushion flowfield established on each side of the biplate, and made up of conductive elements 44. The conductive elements as pins or rods can extend directly through the biplate, or they can have electrical communication with an intermediate electrically conductive element, for example a plate located in the biplate. This pattern defines a flowfield, which is a collection of channels which allow fuel or air to disperse over the electrode. The pattern is not limited to that shown in the figures, but can take on a variety of patterns, regular and nonregular.

An endplate will typically have a flowfield on one of its surfaces, preferably the surface forming a wall of one of the fuel cell compartments. The conductive elements

having a cross section which includes at least one angle which is less than or equal to about 120°.

A particular embodiment of the pincushion flowfield is shown in Fig. 6. In this particular embodiment, conductive elements 44 are rods which are oriented so that angle 72 which is less than about 120° has its apex directed downward. This allows any water which accumulates on the rod to form a droplet at the apex of this angle, and more easily become detached from the conductive element by limiting the amount of adhesion between the growing water droplet and the rod surface.

The pincushion field is present on both sides of the biplate. This can be accomplished by having a single pin pass through the biplate and serve as the contact point for both the anode and cathode. Thus, the pins can be made completely separately from the biplate. The pins are not required to be the same on each side of the biplate. For example, certain embodiments can be constructed so that the pins are longer on one side of the biplate than they are on the other side. Alternatively, the shape of the pins need not be the same on each side of the biplate. Useful pins can be of any conveniently prepared dimension, but good impedences (not more than about 2% of the MEA impedence) are obtained with pins of diameters from about 1/16" to about 1/4". The pins can extend from about 0.2 mm to about 5mm

Alternatively, round "pins" can be made out of a cylindrical rod.

OTHER EMBODIMENTS

It is to be understood that while the invention has been described in conjunction with the detailed description thereof, the foregoing description is intended to illustrate and not limit the scope of the invention, which is defined by the scope of the appended claims. Other aspects, advantages, and modifications are within the scope of the following claims.

4. The assembly of claim 2, wherein the fluorinated polymeric hydrocarbon is a copolymer of tetrafluoroethylene and perfluorinated polyether sulfonic acid.

5. The assembly of claim 1, wherein the conductive elements are arranged in a pincushion array.

6. The assembly of claim 1, wherein the conductive elements comprise graphite.

7. The assembly of claim 1, wherein the conductive elements are rods.

8. The assembly of claim 7, wherein the rods have a cross section comprising an angle of less than or equal to about 120°.

9. The assembly of claim 8, wherein the angle of less than or equal to about 120° is directed downwardly.

10. The assembly of claim 9, wherein the cross section is selected from the group consisting of square, rectangular, diamond-shaped and triangular.

b) an oxidant supply, which supplies an oxidant to at least one surface of at least one plate;

c) a liquid fuel supply, which supplies liquid fuel to at least one surface of at least one plate;and

d) an electrical load which is in electrical contact with the electrically conductive elements of at least two of the plates.

15. A method of generating power with a liquid feed fuel cell system assembly comprising:

a) at least one substantially planar and vertically oriented plate having a hydrophilic surface, a plurality of conductive elements extending from at least one surface of the plate, providing electrical communication through the plate, an air inlet port and an air exit port formed on the plate in locations to establish an air flow path; and a wicking device located at the air exit port, whereby liquid is withdrawn from the air flow path; and

b) operating the fuel cell system in a way that allows water to be removed from the fuel cell.

Fig. 5

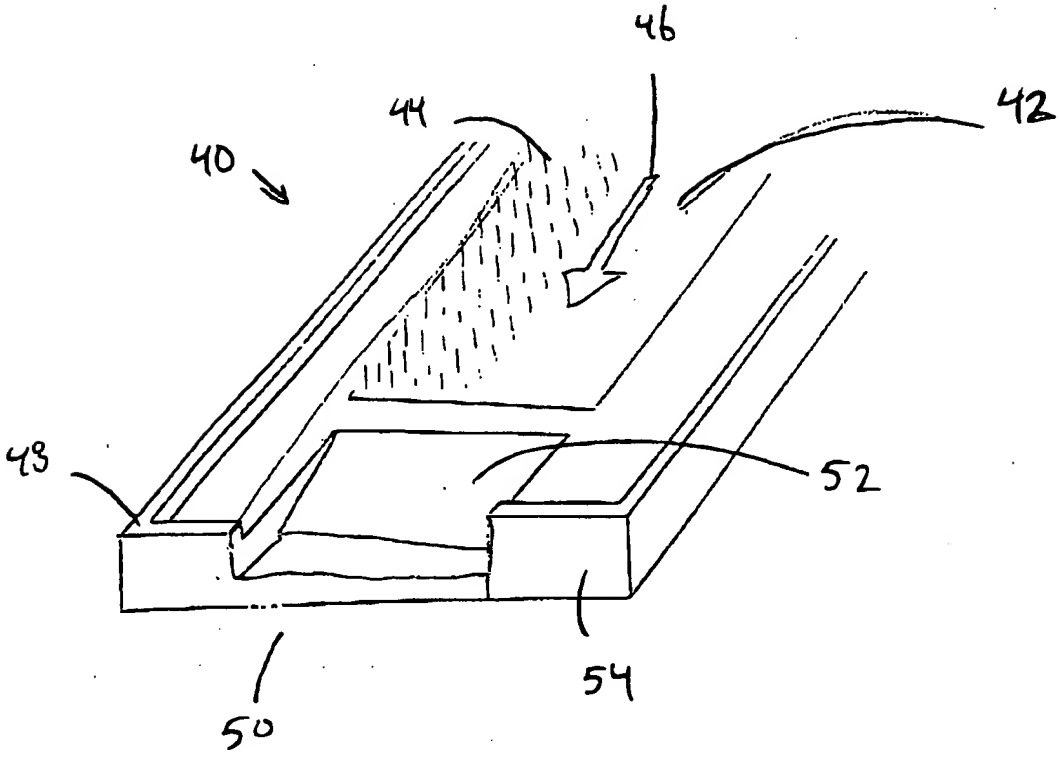


Fig. 6

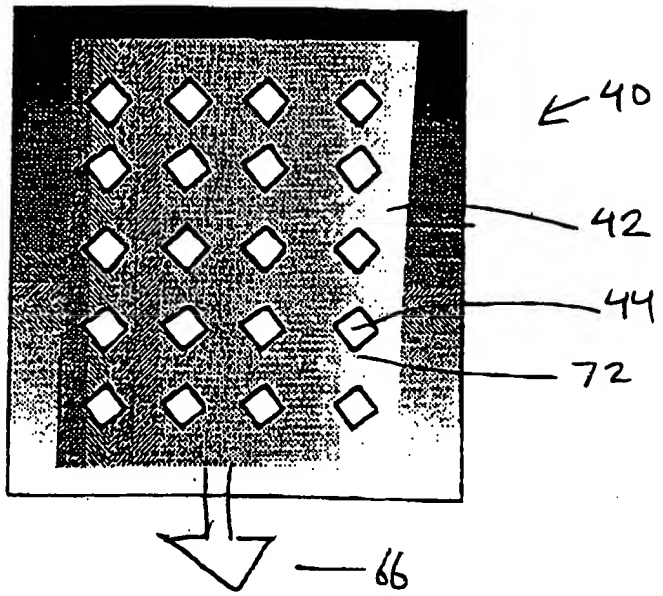
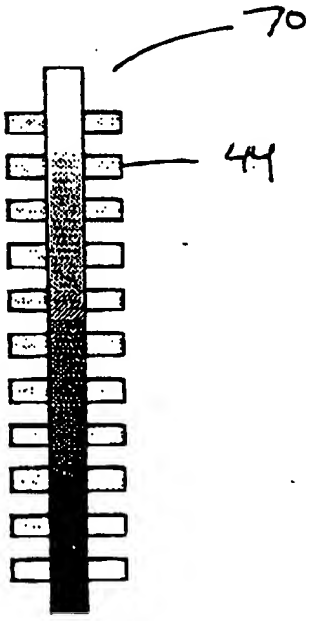


Fig. 7



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/25049

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,880,670 A (SHINN) 29 April 1975, col. 2, lines 25-34, 59-66; col. 3, lines 1-30.	1-15
A	US 5,716,664 A (MARCHETTI) 10 February 1998, all.	1-15
A	US 5,641,586 A (WILSON) 24 June 1997, all.	1-15
A	US 3,418,168 A (WENTWORTH) 24 December 1968, all.	1-15